

**What is claimed is:**

1. A process for preparing a solid highly reactive polyurethane composition containing uretdione groups by mixing

5 A) at least one uretdione-containing curing agent which has a free NCO content of less than 5% by weight and a uretdione content of 1-30% by weight, based on aromatic, aliphatic, (cyclo)aliphatic or cycloaliphatic polyisocyanates and hydroxyl-containing compounds, with a melting point of from 40 to 130°C,

and

10 B) if desired at least one hydroxyl-containing polymer having a melting point of from 40 to 130°C and an OH number of between 20 and 200 mg KOH/gram,

C) in the presence of at least one catalyst

15 C1) of the formula  $M (OR^1)_n (OR^2)_m (OR^3)_o (OR^4)_p (OR^5)_q (OR^6)_r$ , where M is a metal in any positive oxidation state and identical to the sum  $n+m+o+p+q+r$ , m, o, p, q and r are integers from 0 to 6 and the sum  $n+m+o+p+q+r = 1-6$ , the radicals  $R^1-R^6$  simultaneously or independently of one another are hydrogen or alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-8 carbon atoms and the radicals may in each case be linear or branched, unbridged or bridged with other radicals, to form monocyclic, bicyclic or tricyclic systems, and the  
20 bridging atoms may in addition to carbon also be heteroatoms and additionally may have one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and/or

25 C2) comprising tetraalkylammonium salts of the formula  $[NR^1R^2R^3R^4]^+[R^5]^-$ , where  $R^1-R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being in each case linear or branched, unbridged or bridged with other radicals  $R^1-R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1-R^4$  may further  
30 contain one or more alcohol, amino, ester, keto, thio, urethane, urea or

allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is either OH or F,

and/or

- 5 C3) of the formula  $[NR^1R^2R^3R^4]^+ [R^5COO]^-$ , where  $R^1$ - $R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being in each case linear or branched, unbridged or bridged with other radicals  $R^1$ - $R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1$ - $R^4$  may further contain one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is an alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radical, linear or branched, having 1-18 carbon atoms and may further contain one or more alcohol, amino, ester, keto, thio, acid, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms,

15 and/or

- C4) comprising metal acetylacetonates of the formula  $M^{n+} (acac^-)_n$ , where  $M$  = metal ion,  $n$  is a natural number, with  $n = 1-6$ , and  $acac$  is bis(2,4-pentanedionato),

- 20 C5) comprising phosphonium compounds of the formula  $[PR^1R^2R^3R^4]^+ [R^5]^-$ , where  $R^1$ - $R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being in each case linear or branched, unbridged or bridged with other radicals  $R^1$ - $R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1$ - $R^4$  may further contain one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is either OH or F or is  $R^6COO$  where  $R^6$  is synonymous with alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals, linear or branched, having 1-18 carbon atoms and may further contain one or more alcohol, amino, ester, keto, thio, acid, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms,
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so that the fraction of the catalyst under C) is 0.001-5% by weight of the total amount of components A) and, if present, B),

5 D) if desired, a reactive compound which is able to react at elevated temperatures with the acid groups of component B) that may be present and whose fraction is from 0.1 to 10% by weight based on the total amount of A) and, if present, B),

E) if desired, at least one acid in monomeric or polymeric form, in a weight fraction, based on the total formulation, of from 0.1 to 10%,

10 F) if desired, auxiliaries and additives in a mixing apparatus selected from an extruder, intensive kneader, intensive mixer or static mixer, component C) being added subsequently in the mixing apparatus to components A) and, if present, B), D), E) and/or F) already partly or fully mixed in the mixing apparatus and being mixed with the other components and subsequently  
15 isolating the end product by cooling.

2. The process as claimed in claim 1, wherein component C) is added to the mixture after from 10 to 90% of the overall length of the mixing apparatus.

20 3. The process as claimed in claim 1, wherein component C) is added to the mixture after from 20 to 90% of the overall length of the mixing apparatus.

4. The process as claimed in claim 1, wherein component C) is added to the mixture after from 30 to 90% of the overall length of the mixing apparatus.

25 5. The process as claimed in claim 1, wherein component C) is added to the mixture after from 40 to 80% of the overall length of the mixing apparatus.

30 6. The process as claimed in claim 1, wherein component C) is added to the mixture after from 55 to 75% of the overall length of the mixing apparatus.

7. The process as claimed in at least one of the preceding claims, wherein the temperature on addition of component C) is from 70 to 170°C.
8. The process as claimed in at least one of the preceding claims, wherein component A) is based on the polyisocyanates selected from isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), 2-methylpentane diisocyanate (MPDI), 2,2,4-trimethylhexamethylene diisocyanate/2,4,4-trimethylhexamethylene diisocyanate (TMDI), norbornane diisocyanate (NBDI), methylenediphenyl diisocyanate (MDI) and tetramethylxylylene diisocyanate (TMXDI).
9. The process as claimed in at least one of the preceding claims, wherein polyesters, polythioethers, polyethers, polycaprolactams, polyepoxides, polyesteramides, polyurethanes and/or, if desired, low molecular mass di-, tri- and/or tetraalcohols as chain extenders and/or, if desired, monoamines and/or monoalcohols as chain terminators are present as hydroxyl-containing compounds of component A).
10. The process as claimed in at least one of the preceding claims, wherein polyesters, polyethers, polyacrylates, polyurethanes and/or polycarbonates having an OH number of from 20 to 200 mg KOH/gram are present as component B).
11. The process as claimed in at least one of the preceding claims, wherein compounds selected from lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, beryllium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, aluminum hydroxide, zinc hydroxide, lithium methoxide, sodium methoxide, potassium methoxide, magnesium methoxide, calcium methoxide, barium methoxide, lithium ethoxide, sodium ethoxide, potassium ethoxide, magnesium ethoxide, calcium ethoxide, barium ethoxide, lithium propoxide, sodium propoxide, potassium propoxide, magnesium propoxide, calcium propoxide, barium propoxide, lithium isopropoxide, sodium isopropoxide, potassium isopropoxide, magnesium isopropoxide, calcium isopropoxide, barium isopropoxide, lithium 1-butoxide, sodium 1-butoxide, potassium 1-butoxide, magnesium 1-butoxide,

calcium 1-butoxide, barium 1-butoxide, lithium 2-butoxide, sodium 2-butoxide, potassium 2-butoxide, magnesium 2-butoxide, calcium 2-butoxide, barium 2-butoxide, lithium isobutoxide, sodium isobutoxide, potassium isobutoxide, magnesium isobutoxide, calcium isobutoxide, barium isobutoxide, lithium tert-butoxide, sodium tert-butoxide, potassium tert-butoxide, magnesium tert-butoxide, calcium tert-butoxide, barium tert-butoxide, lithium phenoxide, sodium phenoxide, potassium phenoxide, magnesium phenoxide, calcium phenoxide and/or barium phenoxide are present as catalysts C1).

12. The process as claimed in at least one of the preceding claims, wherein compounds selected from methyltributylammonium hydroxide, methyltriethylammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, tetrapentylammonium hydroxide, tetrahexylammonium hydroxide, tetraoctylammonium hydroxide, tetradecylammonium hydroxide, tetradecyltriethylammonium hydroxide, tetraoctadecylammonium hydroxide, benzyltrimethylammonium hydroxide, benzyltriethylammonium hydroxide, trimethylphenylammonium hydroxide, triethylmethylammonium hydroxide, trimethylvinylammonium hydroxide, tetramethylammonium fluoride, tetraethylammonium fluoride, tetrabutylammonium fluoride, tetraoctylammonium fluoride and/or benzyltrimethylammonium fluoride are present as catalysts C2).

13. The process as claimed in at least one of the preceding claims, wherein compounds selected from tetramethylammonium formate, tetramethylammonium acetate, tetramethylammonium propionate, tetramethylammonium butyrate, tetramethylammonium benzoate, tetraethylammonium formate, tetraethylammonium acetate, tetraethylammonium propionate, tetraethylammonium butyrate, tetraethylammonium benzoate, tetrapropylammonium formate, tetrapropylammonium acetate, tetrapropylammonium propionate, tetrapropylammonium butyrate, tetrapropylammonium benzoate, tetrabutylammonium formate, tetrabutylammonium

acetate, tetrabutylammonium propionate, tetrabutylammonium butyrate and/or tetrabutylammonium benzoate are present as catalysts C3).

14. The process as claimed in at least one of the preceding claims, wherein compounds  
5 selected from zinc acetylacetonate and/or lithium acetylacetonate are present as catalysts C4).

15. The process as claimed in at least one of the preceding claims, wherein compounds  
10 selected from tetrabutylphosphonium acetate, tetrabutylphosphonium benzotriazolate, tetrabutylphosphonium hydroxide, ethyltriphenylphosphonium acetate, tetraphenylphosphonium phenoxide, trihexyltetradecylphosphonium decanoate and/or tetrabutylphosphonium fluoride are present as catalysts C5).

16. The process as claimed in at least one of the preceding claims, wherein compounds  
15 selected from triglycidyl ether isocyanurate (TGIC), EPIKOTE 828 (diglycidyl ether based on bisphenol A, Shell), Versatic acid glycidyl esters, ethylhexyl glycidyl ether, butyl glycidyl ether, POLYPOX R 16 (pentaerythritol tetraglycidyl ether, UPPC AG) and other Polypox grades containing free epoxy groups, VESTAGON EP HA 320, (hydroxyalkylamide, Degussa AG), or phenylenebisoxazoline, 2-methyl-2-oxazoline,  
20 2-hydroxyethyl-2-oxazoline, 2-hydroxypropyl-2-oxazoline, 5-hydroxypentyl-2-oxazoline, sodium carbonate and/or calcium carbonate are present as component D).

17. The process as claimed in at least one of the preceding claims, wherein compounds  
25 selected from sulfuric acid, acetic acid, benzoic acid, malonic acid, terephthalic acid, copolyesters and/or copolyamides having an acid number of at least 20 are present as component E).

18. The process as claimed in at least one of the preceding claims, wherein additional  
30 catalysts, leveling agents, light stabilizers, fillers and/or pigments are present as component F).

19. The process as claimed in at least one of the preceding claims, wherein an extruder is used as apparatus.
20. The process as claimed in claim 19, wherein single-screw or multiple-screw extruders, especially twin-screw extruders, planetary roll extruders or annular extruders are used.
21. The process as claimed in at least one the preceding claims, wherein the residence time of the ingredients in the abovementioned apparatus is from 3 seconds to 15 minutes, preferably from 3 seconds to 5 minutes, more preferably from 5 to 180 seconds.
22. The process as claimed in at least one preceding claims, wherein mixing takes place at a temperature below 170°C.
23. A solid highly reactive polyurethane composition containing uretdione groups and obtained by mixing
- A) at least one uretdione-containing curing agent which has a free NCO content of less than 5% by weight and a uretdione content of 1-30% by weight, based on aromatic, aliphatic, (cyclo)aliphatic or cycloaliphatic polyisocyanates and hydroxyl-containing compounds, with a melting point of from 40 to 130°C,
- and
- B) if desired at least one hydroxyl-containing polymer having a melting point of from 40 to 130°C and an OH number of between 20 and 200 mg KOH/gram,
- C) in the presence of at least one catalyst
- C1) of the formula  $M (OR^1)_n (OR^2)_m (OR^3)_o (OR^4)_p (OR^5)_q (OR^6)_r$ , where M is a metal in any positive oxidation state and identical to the sum  $n+m+o+p+q+r$ , m, o, p, q and r are integers from 0 to 6 and the sum  $n+m+o+p+q+r = 1-6$ , the radicals  $R^1-R^6$  simultaneously or independently of one another are hydrogen or alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-8 carbon atoms and the radicals may in each case be linear or branched, unbridged or bridged with other radicals, to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms and additionally

may have one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and/or

5 C2) comprising tetraalkylammonium salts of the formula  $[NR^1R^2R^3R^4]^+[R^5]^-$ , where  $R^1$ - $R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being in each case linear or branched, unbridged or bridged with other radicals  $R^1$ - $R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1$ - $R^4$  may further  
10 contain one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is either OH or F, and/or

15 C3) of the formula  $[NR^1R^2R^3R^4]^+[R^5COO]^-$ , where  $R^1$ - $R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being in each case linear or branched, unbridged or bridged with other radicals  $R^1$ - $R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1$ - $R^4$  may further contain one or more alcohol,  
20 amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is an alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radical, linear or branched, having 1-18 carbon atoms and may further contain one or more alcohol, amino, ester, keto, thio, acid, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms,  
25 and/or

C4) comprising metal acetylacetonates of the formula  $M^{n+}(acac^-)_n$ , where  $M$  = metal ion,  $n$  is a natural number, with  $n = 1-6$ , and  $acac$  is bis(2,4-pentanedionato),

30 C5) comprising phosphonium compounds of the formula  $[PR^1R^2R^3R^4]^+[R^5]^-$ , where  $R^1$ - $R^4$  simultaneously or independently of one another are alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals having 1-18 carbon atoms and being



in each case linear or branched, unbridged or bridged with other radicals  $R^1$ - $R^4$ , to form monocyclic, bicyclic or tricyclic systems, and the bridging atoms may in addition to carbon also be heteroatoms, and each radical  $R^1$ - $R^4$  may further contain one or more alcohol, amino, ester, keto, thio, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms, and  $R^5$  is either OH or F or is  $R^6$ COO where  $R^6$  is synonymous with alkyl, aryl, aralkyl, heteroaryl or alkoxyalkyl radicals, linear or branched, having 1-18 carbon atoms and may further contain one or more alcohol, amino, ester, keto, thio, acid, urethane, urea or allophanate groups, double bonds, triple bonds or halogen atoms,

so that the fraction of the catalyst under C) is 0.001-5% by weight of the total amount of components A) and, if present, B),

D) if desired, a reactive compound which is able to react at elevated temperatures with the acid groups of component B) that may be present and whose fraction is from 0.1 to 10% by weight based on the total amount of A) and, if present, B),

E) if desired, at least one acid in monomeric or polymeric form, in a weight fraction, based on the total formulation, of from 0.1 to 10%,

F) if desired, auxiliaries and additives

in a mixing apparatus selected from an extruder, intensive kneader, intensive mixer or static mixer, component C) being added subsequently in the mixing apparatus to components A) and, if present, B), D), E) and/or F) already partly or fully mixed in the mixing apparatus and being mixed with the other components and subsequently isolating the end product by cooling.

24. The solid highly reactive polyurethane composition containing uretdione groups as claimed in claim 23, comprising compounds A) to F) as set forth in at least one of claims 2 to 22.

25. The use of a solid polyurethane composition containing uretdione groups and prepared as set forth in at least one of claims 1 to 22, curing at a low baking temperature, for producing a powder coating material.